

to recover the alkyltrichlorosilanes present. Reduction of the alkyltrichlorosilanes followed by distillation yielded a product with boiling point 134–136°. Gas chromatographic and infrared analyses indicated that the composition was identical to that obtained by reduction of the starting material.

Incomplete Addition of Trichlorosilane to 1-Methylcyclohexene.—The addition of trichlorosilane to 1-methylcyclohexene in the presence of chloroplatinic acid was interrupted after 4 hours and distilled to yield unreacted olefin and (cyclohexylmethyl)-trichlorosilane. On the basis of gas chromatography, the olefin was shown to be a mixture of 95% 1-methylcyclohexene and 5% 4-methylcyclohexene.

Attempted Isomerization of 1-Methylcyclohexene in the Presence of Chloroplatinic Acid.—In a 25-ml. flask was placed 5 g. (0.05 mole) of 1-methylcyclohexene and 0.02 g. of chloroplatinic acid as a solution in 0.5 ml. of isopropyl alcohol. The mixture was heated at 55° for a period of 48 hours then analyzed by gas chromatography. No isomerization had taken place.

Attempted Isomerization of 4-Methylcyclohexene in the Presence of Chloroplatinic Acid.—A mixture of 9.6 g. (0.1 mole) of 4-methylcyclohexene and 0.05 g. of chloroplatinic acid in 0.5 ml. of isopropyl alcohol was refluxed for 50 hours. Gas chromatographic and infrared analyses of the olefin showed that no isomerization had taken place. The attempt was repeated in the presence of SiCl_4 with the same result.

Platinum-catalyzed Addition of Trichlorosilane to 1-Methylcyclohexene Using *n*-Hexane as Solvent.—To a mixture of 51 g. (0.38 mole) of trichlorosilane and 0.05 g. of chloroplatinic acid in 0.5 ml. of isopropyl alcohol was added 19.2 g. (0.2 mole) of 1-methylcyclohexene and 17.2 g. (0.2 mole) of *n*-hexane (Phillips Petroleum). The mixture was refluxed for 26 hours during which time the pot temperature rose from 56° to 64°. Excess trichlorosilane and *n*-hexane were removed by distillation leaving 44 g. (78%) of

adduct. Lithium aluminum hydride reduction of the adduct provided only (cyclohexylmethyl)-silane.

Platinum-catalyzed Addition of Trichlorosilane to 1-Methyl- d_3 -cyclohexene.—In a 125-ml. three-necked flask was placed 5.0 g. (0.05 mole) of 1-methyl- d_3 -cyclohexene, 91 g. (0.67 mole) of trichlorosilane and 0.05 g. of chloroplatinic acid in 0.5 ml. of isopropyl alcohol. The mixture was refluxed under an extra pressure of nitrogen for 42 hours to ensure complete reaction. The excess trichlorosilane was removed by distillation, but because only a small amount of adduct was obtained (5 g.) the reduction step was carried out without further purification. The reduction of the adduct was conducted in the usual manner with excess lithium aluminum hydride followed by hydrolysis and distillation. In addition to unreacted olefin, there was obtained 1.7 g. (26%) of silanes boiling at 140–145°. Gas chromatography showed that two isomeric silanes were present in a 1:1 ratio. The first component, n^{25p} 1.4505, had a retention time corresponding to *trans*-1-methyl-2-silylcyclohexane.⁸ The second component, n^{25p} 1.4550, had a retention time corresponding to the terminal adduct (cyclohexylmethyl)-silane. These components were isolated by preparative gas chromatography and analyzed for deuterium content by the method described earlier in this section. The similarities of the retention times and refractive indices with the non-deuterated standards characterize these products as *trans*-1-methyl- d_3 -2-silylcyclohexane and (cyclohexylmethyl- d_3)-silane.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{D}_3\text{Si}$: D, 4.6. Found: *trans* isomer, D, 4.5, 4.5; terminal adduct, D, 4.4, 4.4.

Acknowledgment.—The authors wish to express their appreciation to Hsien-Ying Niu for assistance in the deuterium analyses and to Dr. William H. Glaze for assistance in obtaining and interpreting the n.m.r. spectra.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, AGRICULTURAL CHEMICALS DIVISION, MONSANTO CHEMICAL CO., ST. LOUIS 66, MO.]

Reaction of Phosphorus Compounds. IV. Haloenamines and Imidoyl Chlorides from Reaction of Phosphines with Haloamides

BY A. J. SPEZIALE AND L. R. SMITH

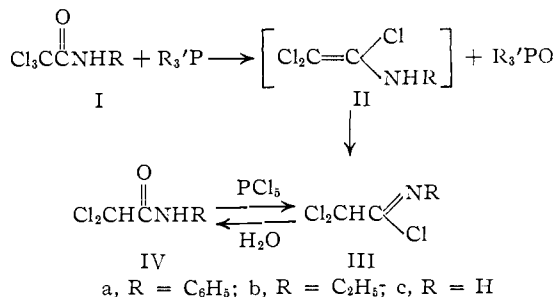
RECEIVED SEPTEMBER 20, 1961

The reaction of trivalent phosphorus compounds with trichloroacetamides has been extended to *N*-monosubstituted trichloroacetamides and to trichloroacetamide. The products are imidoyl chlorides or dichloroacetone nitrile, respectively. Extension of the reaction to α -substituted dichloroacetamides appears limited and depends on the electrical effects of the substituents on the α -carbon and the nitrogen atom. The reaction in one case led to a diposponium enamine. Reaction of α -chloroacetamides with phosphines leads to α -phosphonium salts. The mechanism of the reaction leading to haloenamines is discussed and generalized.

The reaction of trialkyl phosphites or tertiary phosphines with *N,N*-dialkyl or *N,N*-diaryl-2,2,2-trichloroacetamides has been shown to yield *N,N*-dialkyl or *N,N*-diaryl-1,2,2-trichlorovinylamines.¹ The reaction has now been extended to alkyl or aryl monosubstituted trichloroacetamides (I). The products in these cases are dichloroacetimidoyl chlorides (III). Treatment of 2,2,2-trichloroacetanilide (Ia) with tributylphosphine gave a 33% yield of *N*-phenyl-2,2-dichloroacetimidoyl chloride (IIIa). Similarly, reaction of *N*-ethyl-2,2,2-trichloroacetamide (Ib) with triphenylphosphine gave *N*-ethyl-2,2-dichloroacetimidoyl chloride (IIIb) in 46% yield. These imidoyl chlorides were identical with those obtained by the action of phosphorus pentachloride on the corresponding dichloroacetamides (IV). The *N*-phenyl- and *N*-ethylimidoyl chlorides (IIIa,b) were rapidly hydrolyzed to the

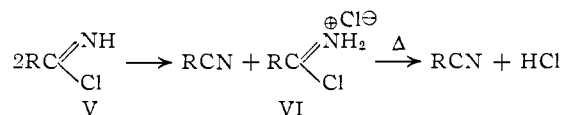
corresponding dichloroacetamides (IVa,b) on treatment with water.

It is presumed that IIIa and IIIb are formed *via* a mechanistic route similar to that which produces the vinylamines in the case of disubstituted trichloroacetamides. However, in the monosubstituted case the supposed intermediate enamine II can tautomerize to the more stable imidoyl chloride III.

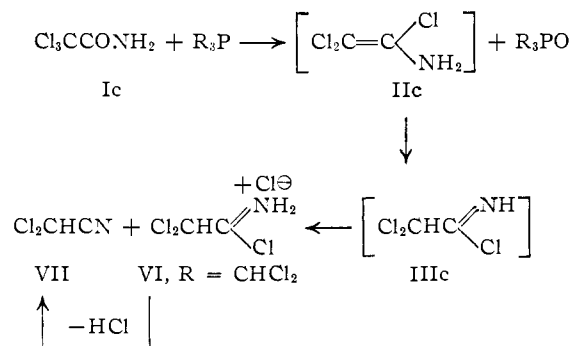


(1) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 (1960).

In light of the reactions of monosubstituted trichloroacetamides, the reaction of trichloroacetamide (Ic) with a tertiary phosphine might be expected to yield dichloroacetimidoyl chloride (IIIc). However, it has been shown that unsubstituted imidoyl chlorides (V) are unstable and that they disproportionate into the nitrile and the hydrochloride of the imidoyl chloride (VI).² An imidoyl chloride hydrochloride is also unstable and on heating decomposes to the nitrile and hydrogen chloride.²



Treatment of trichloroacetamide (Ic) with triphenylphosphine led to a fuming liquid which, when washed with sodium bicarbonate solution, yielded dichloroacetoneitrile. When the fuming liquid was left in a Dry Ice trap in moist air, dichloroacetamide (IVc) was produced. The mixture formed on treatment of dichloroacetoneitrile with hydrogen chloride, when left in moist air, also yielded dichloroacetamide (IVc). Thus, treatment of trichloroacetamide (Ic) with triphenylphosphine leads to dichloroacetoneitrile (VII) and the imidoyl chloride hydrochloride (VI, R = CHCl₂). These products are undoubtedly formed *via* the unstable enamine IIC.



In the trichloroacetamide series, only the N,N-aralkyltrichloroacetamides remained to be investigated. Treatment of N-methyl-2,2,2-trichloroacetamide with triphenylphosphine gave a 60% yield of N-methyl-N-phenyl-1,2,2-trichlorovinylamine (VIII). The vinylamine was hydrolyzed to N-methyl-2,2-dichloroacetamide on treatment with water.

Since the chloride migration reaction appears to be general for 2,2,2-trichloroacetamides, it was decided to investigate the reaction when one of the chlorine atoms is replaced by a different group.³

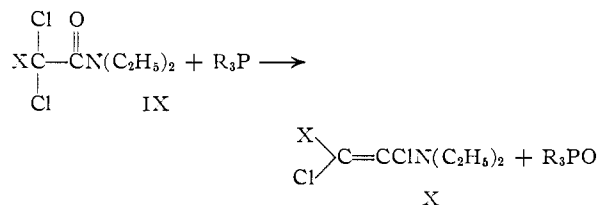
Treatment of N,N-diethyl-2,2-dichloro-2-fluoroacetamide (IXa) with tributylphosphine at 125–130° for 2 hr. led to a 13% yield of N,N-diethyl-1,2-dichloro-2-fluorovinylamine.⁴ In contrast, the

(2) F. Klages and W. Grill, *Ann.*, **594**, 21 (1955).

(3) N,N-Diethyl-2,2,2-trifluoroacetamide failed to react with tributylphosphine on heating at 155–160° for 4 hours. Treatment of N,N-diethyl-2,2,2-tribromoacetamide with tributylphosphine apparently led to the tribromovinylamine. The enamine in this case was too unstable to be completely characterized. The infrared spectrum of the crude product exhibited infrared absorption at 6.21 μ (C=C) and hydrolysis led to N,N-diethyl-2,2-dibromoacetamide.

reaction of N,N-diethyl-2,2,2-trichloroacetamide with tributylphosphine proceeds exothermally at room temperature to give a 74% yield of the trichlorovinylamine.¹

Reaction of N,N-diethyl-2,2-dichloropropionamide (IXb) with tributylphosphine at 160–170° for 1 hour did not produce any enamine and gave only a partial recovery of starting material.⁴

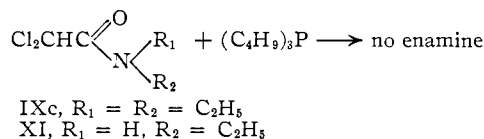


- a, X = F; c, X = H
b, X = CH₃; d, X = C₆H₅
e, X = Cl

In contrast to the foregoing cases, treatment of N,N-diethyl-2,2-dichlorophenylacetamide (IXd) with tributylphosphine or triphenylphosphine led to a high yield of N,N-diethyl-α,β-dichlorostyrylamine (Xd).

Vapor phase analysis of Xd indicated the presence of only one component. If both the *cis* and *trans* isomers were formed, they could not be separated by gas chromatography.

Reaction of N,N-diethyl-2,2-dichloroacetamide (IXc) and N-ethyl-2,2-dichloroacetamide (XI) with tributylphosphine did not produce any enamine.⁴



Since it appears that the chloride migration reaction is facilitated by electron-withdrawing

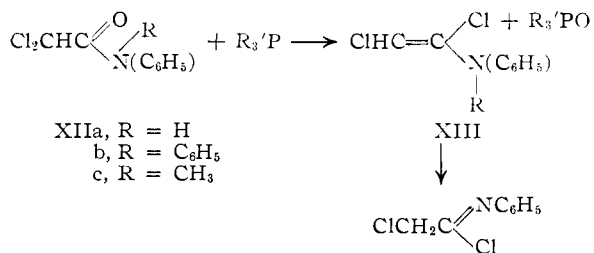
(4) The viscous residues after distillation were found to be water soluble and the aqueous solution gave a positive test for chloride ion. Significant infrared absorptions of the residues were found at: IXa (3% CHCl₃), 4.07, 6.12 μ; IXb (3% CHCl₃), 4.05, 6.12 μ; IXc (film), 6.00, 6.13, 6.37 μ; XI (film), 5.92, 6.03, 6.13 μ. These absorptions compare with the carbonyl absorption of the starting amides as follows: IXa (film), 5.95 μ; IXb (film), 6.02 μ; IXc (3% CHCl₃), 6.00 μ; XI (3% CHCl₃), 6.02 μ.

The infrared absorption at 6.12 μ in the first two cases would seem to indicate a carbon-carbon double bond rather than a carbonyl group. The shifts from 5.95 and 6.02 μ to 6.12 μ (amide IXa, IXb to residue IXa, IXb) are in the opposite direction from that expected if a carbonyl compound were present in the residue. A phosphonium group bonded at the α-carbon atom would be expected to shift the carbonyl absorption to lower wave lengths. In order to determine the actual effect of an α-phosphonium group on amide carbonyl absorption, N,N-diethyl-2-chloroacetamide was treated with tributylphosphine. The infrared spectrum of the product exhibited carbonyl absorption at 6.22 μ as compared with 6.14 μ in the spectrum of the starting amide—a shift in the direction expected and opposite from the above cases. Treatment of the product with phenyllithium followed by reaction with benzaldehyde gave a high yield of N,N-diethylcinnamamide showing that the phosphorus was bonded at the α-carbon atom. This is one of the few cases where a purely aliphatic ylid has been found to undergo a normal Wittig reaction. See: (a) G. Wittig, *Angew. Chem.*, **68**, 505 (1956); (b) A. W. Johnson and R. B. Lacount, *Tetrahedron*, **9**, 130 (1960); (c) A. W. Johnson, *J. Org. Chem.*, **25**, 183 (1960); (d) A. W. Johnson and R. B. Lacount, *J. Am. Chem. Soc.*, **83**, 417 (1961); (e) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961).

In light of these facts, it appears that the reaction of tributylphosphine with IXa and IXb leads to phosphonium salts containing carbon-carbon double bonds. The reaction of tributylphosphine with IXc and XI appears complex.

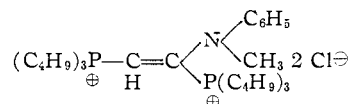
groups bonded at the α -carbon atom of the amide, an investigation was conducted to determine if electron-withdrawing groups bonded at the amide nitrogen atom would also facilitate the reaction.

In contrast to the failure of the chloride migration reaction with *N,N*-diethyl-2,2-dichloroacetamide (IXc), treatment of *N,N*-diphenyl-2,2-dichloroacetamide (XIId) with triphenylphosphine gave an 84% yield of *N,N*-diphenyl-1,2-dichlorovinylamine (XIIIb). The reaction was extended to

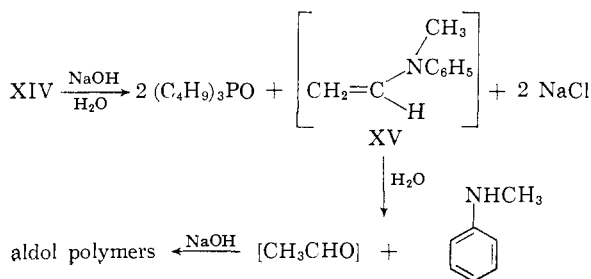


2,2-dichloroacetanilide (XIIa) and *N*-methyl-2,2-dichloroacetanilide (XIIc). Compound XIIa was converted directly to the imidoyl chloride *via* the enamine XIIIa. The enamine XIIIc was formed in very low yield in the case of XIIc and was so unstable that an adequate elemental analysis was not obtained. It was, however, characterized by its infrared spectrum and by hydrolysis to *N*-methyl-2-chloroacetanilide. The residue, after distillation of the enamine, tributylphosphine oxide and starting amide, yielded a yellow crystalline solid.

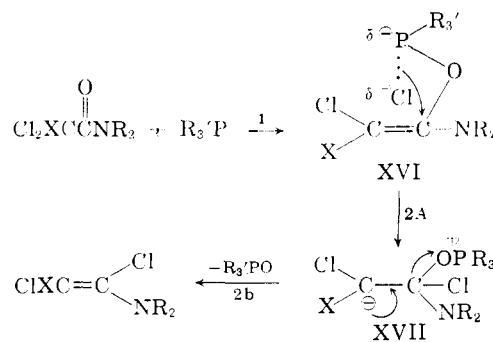
The elemental analysis of the yellow solid showed that it did not contain oxygen. The analysis supported a structure of the type



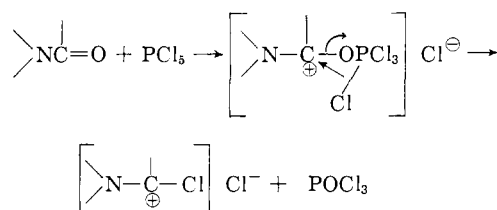
This structural assignment for XIV was further supported by its solubility in water, the presence of two ionic chlorine atoms and by its infrared spectrum. The infrared spectrum (3% CHCl_3) exhibited absorption at 4.05μ which may be attributed to a positively charged phosphorus atom and at 6.27μ which must be attributed to the presence of a carbon-carbon double bond. In order to study the infrared spectrum of a phosphonium salt, tetrabutylphosphonium bromide was prepared. The infrared spectrum of the latter compound had an absorption band at 4.10μ which appears to be associated with positively charged phosphorus. Hydrolysis of XIV led to *N*-methylaniline and tributylphosphine oxide. The *N*-methylaniline may be formed from the enamine XV.



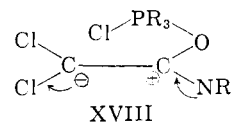
The mechanism of the migration reaction is formulated as proceeding *via* the intermediate ion pair XVI.



Step 2a is similar to the second step in the formation of amide chlorides from the reaction of amides with phosphorus pentachloride.⁵



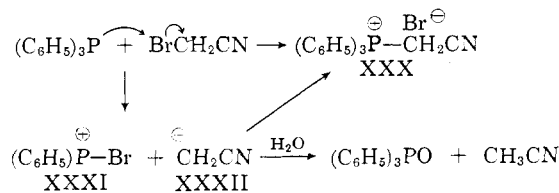
When viewed in this manner it is evident why only haloamides have been made to undergo the migration reaction. The ability of the amide nitrogen atom (and of the α -chlorine atoms) to stabilize resonance forms of the type XVIII is probably an important factor. Step 2b would undoubtedly be very fast and steps 2a and 2b are perhaps best viewed as being concerted.



Steps 2a and 2b are also analogous to the reaction which occurs when the triphenyl phosphite-benzil adduct (XIX) is treated with hydrogen chloride.^{6a}

(5) H. Eilingsfeld, M. Seefelder and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

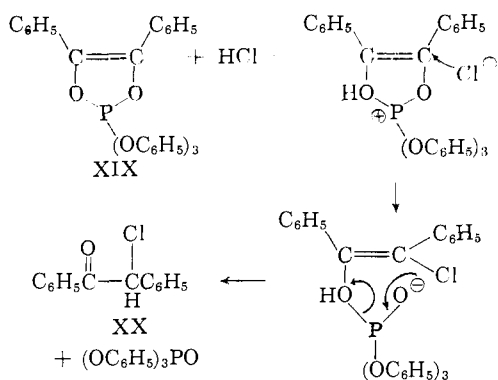
(6) (a) F. Ramirez and N. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960), and references therein; (b) Good evidence for the attack of a tertiary phosphine on a halogen atom is found in the work of P. Schiemenz and H. Englehard [*Ber.*, **94**, 578 (1961)]. These workers report, without extensive interpretation, that treatment of bromoacetonitrile with triphenylphosphine under anhydrous conditions led to the normal phosphonium salt XXX.



Treatment of bromoacetonitrile with triphenylphosphine in moistened chloroform, however, did not give XXX but only triphenylphosphine oxide and acetonitrile. It was further reported that the phosphonium salt XXX was stable to boiling water.

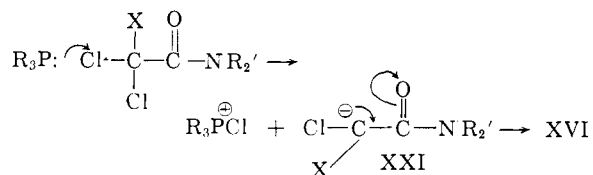
We interpret these results as good evidence for the presence of the intermediates XXXI and XXXII. Under anhydrous conditions they

Generally this reaction leads to products of the Perkow type (α -ketol monophosphates or α -



quinol monophosphates) but in this one case, where the phenyl groups can facilitate attack by chloride ion at an olefinic carbon atom, desyl chloride (XX) is formed exclusively.

The initial attack of the phosphine on the chloroamide to form XVI may occur at the carbonyl carbon atom, the carbonyl oxygen atom, the α -carbon atom or on a chlorine atom. We feel that steric factors rule out attack at the α -carbon atom and at the carbonyl carbon atom. Of the two remaining points of attack, the oxygen atom (as was favored in paper II of this series) or a chlorine atom, we feel that attack on a chlorine atom^{6a} better explains the reluctance of *N,N*-diethyl-2,2-dichloro-2-fluoroacetamide to undergo the reaction. The major difference in the fluorine and chlorine substituents is the ability of the latter to stabilize a negative charge.⁷ Thus, some step in the reaction path must involve the formation of a negative charge at the α -carbon atom. The charge can be generated either by attack at the chlorine atom to give the enolate XXI or by conversion of XVI to XVII (step 2a). If oxygen attack occurred (giving XVI directly) charge formation would take place only in step 2a and some intermediate should be formed irreversibly and starting material should not be recovered. The formation of a negative charge on the α -carbon atom would occur in the first step of the reaction if initial attack occurred on a chlorine atom. Under



conditions where trichloroamides react readily and in high yield, the fluorodichloroamide was recovered unchanged. To explain these results,

combine to form the stable phosphonium salt XXX but, in the presence of water, they are hydrolyzed to triphenylphosphine oxide and acetonitrile.

D. B. Denny (abstracts and oral presentation, Div. of Org. Chem. A.C.S. Meeting, Chicago, Ill., Sept., 1961, p. 95Q) has found similar results and applies a similar interpretation in the reaction of *t*-butyl hypochlorite with triphenylphosphine in the presence and absence of methanol.

(7) J. Hine, M. W. Burske, M. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

the charge formation must take place in the first step and this can only occur if the initial reaction involves chlorine rather than oxygen attack.

The failure of the fluorodichloroamide (IXa), the dichloropropionamide (IXb) and the dichloroacetamide (IXc) to undergo the reaction in high yield, while the dichlorophenylacetamide (IXd) and the trichloroacetamide (IXe) undergo the reaction with ease, may be explained on the basis of the ability of a chlorine atom or a phenyl group to stabilize a negative charge on the α -carbon atom while a fluorine atom, a methyl group or a hydrogen atom cannot do so. This fact may be explained on the basis of the ability of the former groups to delocalize electrons through resonance. The latter groups cannot participate in this type of resonance.

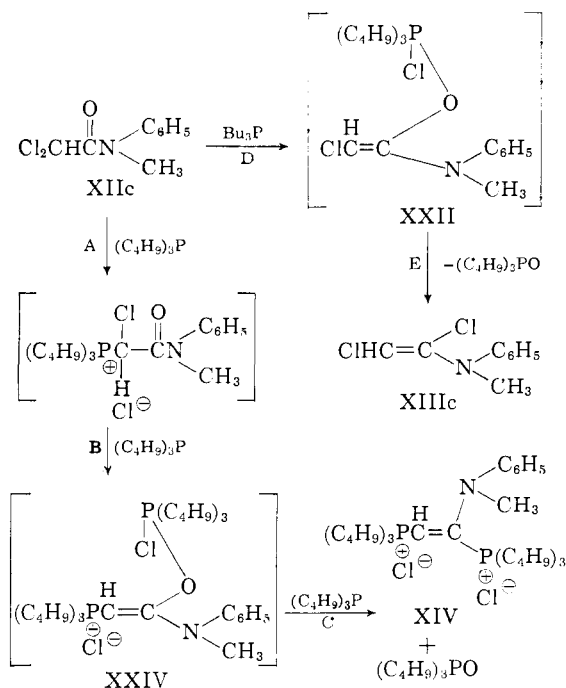


The proposed mechanism of the chloride migration reaction proceeds *via* the nucleophilic attack of chloride ion on the 1-carbon atom (step 2). If the chloride ion is actually present as a free species, reaction in the presence of bromide ion should lead to the isolation of some *N,N*-diethyl-1-bromo-1,2-dichlorovinylamine. Reaction of *N,N*-diethyl-2,2,2-trichloroacetamide and tributylphosphine in chloroform solution in the presence of a molar equivalent of tetrapropylammonium bromide did not lead to a significant amount of volatile, bromine-containing products—if any.⁸ Vapor phase analysis showed the presence of a very reactive substance of unknown structure, but the material decomposed before it could be characterized. In addition, the yield of *N,N*-diethyl-1,2,2-trichlorovinylamine was drastically reduced under these conditions; the yield of the enamine amounted to only 16% after 7 hr. at 85°. This effect is not completely due to the chloroform solvent since enamine is formed in 57% yield when the reaction is run in chloroform in the absence of tetrapropylammonium bromide. The reduction of yield in the presence of tetrapropylammonium bromide appears to be a salt effect and may indicate destruction of charge in some step of the chloride migration reaction. We must conclude that if the reaction proceeds *via* the proposed mechanism, the chloride ion is never far enough removed from the positively charged phosphorus atom to exchange with bromide ion to a significant degree. These results indicate that XVI should be viewed as an ion pair.

When the reaction is run in a polar medium, steps 2a and 2b would be slower than when no solvent is used. Tributylphosphine in preference to chloride ion may then displace the phosphine oxide moiety. This would account for the reduction in yield of enamine when the reaction is run in chloroform and the drastic reduction in yield in the presence of tetrapropylammonium bromide.

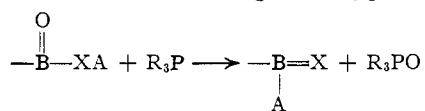
(8) The bromine determination on all of the volatile products would have detected bromine in a concentration greater than 1%.

In the case of the N-alkyldichloroacetamides, where positive halogen attack is less favorable and where nucleophilic displacement of an α -chlorine is facilitated, reaction with a tertiary phosphine may produce an α -phosphonium salt. The introduction of the electron-withdrawing α -phosphonium group may then facilitate positive chlorine attack. The formation of XIV from XIIc may be explained on this basis. Since the attack of



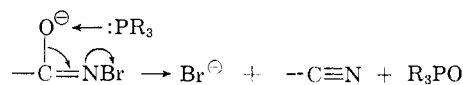
chloride ion on the 1-carbon atom would be expected to be slow in the case of XXIV because of the lack of carbanion stabilization at the α -carbon atom, the more nucleophilic tributylphosphine (some of which is present since steps a and d would be slow) can displace tributylphosphine oxide—finally yielding XIV. The driving force for step c (and for step E) is probably the ease with which a stable tributylphosphine oxide moiety can be displaced. Such a displacement could also occur in the case of XXII if E were not a fast step. Reaction of 3 moles of tributylphosphine with one mole of amide led to a 54% yield of XIV. It is doubtful that the diposphonium enamine is formed *via* the dichloroenamine XIIIc since under similar conditions N,N-diphenyl-1,2-dichlorovinylamine, which should be even more prone to attack by phosphine, does not react with tributylphosphine.

The chloride migration reaction is related to several other reactions of the general type

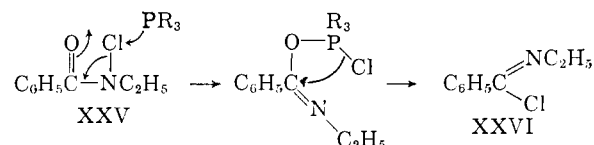


For example, the treatment of N-bromoamides with triphenylphosphine has been reported to yield nitriles. Trippett and Walker⁹ have proposed a mechanism for this reaction which involves enolization of the bromoamide. The chloride

(9) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 2976 (1960).

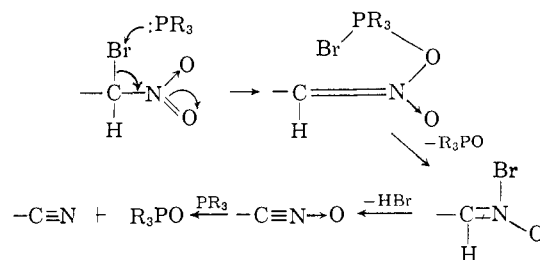


migration reaction cannot proceed by this mechanism since N,N-diethyl-2,2,2-trichloroacetamide cannot undergo enolization. In order to test the mechanism of Trippett and Walker, the reaction of N-chloro-N-ethylbenzamide (XXV) (which cannot enolize) with triphenylphosphine was studied. This reaction was found to yield N-ethylbenzimidoyl chloride (XXVI). This is consistent with the proposed mechanism of the chloride migration reaction and rules out any mechanism involving enolization.

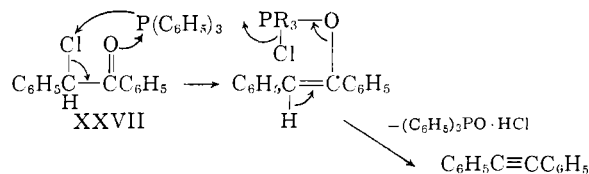


The isolation of nitriles from the reaction of unsubstituted N-haloamides can be explained on the basis of the decomposition of the unstable unsubstituted imidoyl chlorides which would be formed.² This would be in agreement with the work reported earlier concerning the reaction of 2,2,2-trichloroacetamide with triphenylphosphine.

The reaction of α -bromonitroalkanes with phosphines⁹ to yield nitriles is also of the same general type and a similar mechanism may be written for this reaction which does not involve an acinitro form.

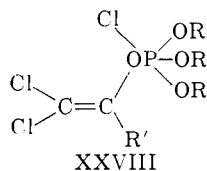


Finally, the reaction of α -phenylphenacyl chloride (XXVII) with triphenylphosphine to yield diphenylacetylene⁹ is of this general type.

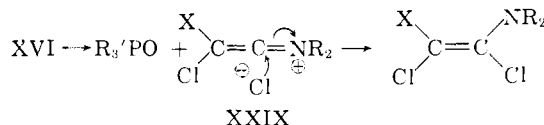


We feel that the Perkow reaction^{1,10} and reaction of phosphites with trichloroamides¹ also proceed *via* a mechanism which is quite analogous to these reactions, *i.e.*, initial attack of phosphorus on chlorine. In the case of the reaction of trichloroaldehydes and esters with phosphites, the intermediate XXVIII reacts by way of chloride ion displacing a phosphite alkyl group and yields the vinyl phosphate and alkyl chloride (the Perkow reaction). In the case of the reaction of trichloro-

(10) W. Perkow and K. Knoevnagel, *Ber.*, **88**, 662 (1955).



amides with phosphites, the intermediate [XXVIII, $R' = NR_2''$] reacts by way of chloride ion attacking the 1-carbon atom and displacing trialkylphosphate. The role of the nitrogen atom in promoting the latter displacement is obvious if one considers a resonance form of the type XVIII. Finally, it is possible that the electron pair on nitrogen may displace the phosphate moiety and the resulting ketenimine XXIX may react with chloride ion to form the enamine.



Experimental¹¹

Tributylphosphine was obtained from Food Machinery Corp. Triphenylphosphine was obtained from Eastman Kodak Co. N-Substituted mono-, di- and trichloroacetamides were prepared from Eastman Kodak Co. mono-, di- or trichloroacetyl chlorides and the appropriate amines.

N-Phenyl-2,2-dichloroacetimidoyl Chloride (IIIa).—A mixture of 2,2,2-trichloroacetanilide (47.7 g., 0.2 mole) and benzene (200 ml.) was stirred at room temperature while tributylphosphine (40.5 g., 0.2 mole) was added dropwise. The exothermic reaction was controlled by adding the tributylphosphine at such a rate that the temperature was kept below 40°. The solution was stirred for 2 hr. after the completion of the addition, and then heated at 50° for 0.5 hr. The benzene was removed *in vacuo* and distillation produced a yellow liquid which on redistillation gave colorless N-phenyl-2,2-dichloroacetimidoyl chloride (14.6 g., 0.065 mole, 33%), b.p. 83–86° (0.5 mm.), n_D^{25} 1.5665; reported b.p. 127–129° (14 mm.),¹² 115–117° (10 mm.),¹ n_D^{25} 1.5723.¹ Further distillation gave tributylphosphine oxide (36.8 g., 0.13 mole, 65%), b.p. 127–130° (0.4 mm.); reported b.p. 104° (0.04 mm.),¹ 185–186° (18 mm.).¹³ The infrared spectrum was identical with that of an authentic sample.¹

A mixture of N-phenyl-2,2-dichloroacetimidoyl chloride (IIIa, 2.35 g., 0.0106 mole) and water (20 ml.) was warmed at 50° for 0.5 hr. The mixture was extracted with ether (125 ml.). The aqueous solution was found to contain chloride ion (0.00975 mole, 92%, by potentiometric titration). The ethereal extract was dried over anhydrous magnesium sulfate and evaporated to a small volume. Chilling and addition of hexane separated 2,2-dichloroacetanilide (1.96 g., 91%), m.p. 124–126°, reported¹⁴ m.p. 119°. The infrared spectrum was identical with that of an authentic sample and there was no depression of a mixed melting point.

N-Ethyl-2,2-Dichloroacetimidoyl Chloride (IIb).—A solution of triphenylphosphine (52.4 g., 0.2 mole) in hexane (200 ml.) was heated to 60° and N-ethyl-2,2,2-trichloroacetamide (38.1 g., 0.2 mole) was added in small portions. The solution was refluxed for 1 hr. and then the hexane was removed *in vacuo*. Distillation produced N-ethyl-2,2-dichloroacetimidoyl chloride as a colorless liquid (16.1 g., 0.092 mole, 46%), b.p. 72° (3 mm.), n_D^{25} 1.4792; reported¹⁵ b.p. 161–164°. The infrared spectrum was identical with that of an authentic sample prepared from N-ethyl-2,2-dichloroacetamide and phosphorus pentachloride.¹⁵ The

residue was dissolved in methanol and filtered through charcoal. The addition of water separated a tan solid. Recrystallization from benzene–hexane gave triphenylphosphine oxide (42.1 g., 0.15 mole, 75%), m.p. 155–156°, reported m.p. 156.4–157.2°. The infrared spectrum was identical with that of an authentic sample.¹

A mixture of N-ethyl-2,2-dichloroacetimidoyl chloride (1.50 g., 0.0086 mole) and water (20 ml.) was allowed to stand for 1 hr. and then was extracted with ether (2 × 50 ml.). The aqueous solution was found to contain chloride ion (0.0086 mole, 100%, by potentiometric titration.). The ethereal solution was dried over anhydrous magnesium sulfate and evaporated to a small volume. Chilling and the addition of hexane separated N-ethyl-2,2-dichloroacetamide (0.91 g., 0.0058 mole, 67%), m.p. 59°, reported¹⁶ m.p. 59°. The infrared spectrum was identical with that of an authentic sample and there was no depression of mixed melting point.

Reaction of 2,2,2-Trichloroacetamide and Triphenylphosphine.—A flask containing 2,2,2-trichloroacetamide (32.5 g., 0.2 mole) and triphenylphosphine (52.4 g., 0.2 mole) was attached to vacuum pump (0.2 mm.) through a Dry Ice trap. The mixture was heated slowly to 50° and the temperature rose rapidly to 80°. The reaction was controlled with an ice-bath. After the temperature had moderated, the mixture was heated at 65–80° for 1 hr. Hydrogen chloride was evolved. The Dry Ice trap was found to contain a fuming liquid (7.5 g.). The liquid was dissolved in ether (50 ml.) and the ethereal solution was washed with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate and the ether was distilled. Further distillation gave dichloroacetoneitrile (6.2 g., 0.058 mole, 29%), b.p. 112°, reported¹⁶ b.p. 112°. The infrared spectrum was identical with that of an authentic sample.¹⁷

The residual fuming liquid in the Dry Ice trap solidified on standing. The solid was dissolved from the Dry Ice trap with methylene chloride. The solution was evaporated to a small volume and the addition of hexane separated 2,2-dichloroacetamide (0.11 g., 0.00086 mole, 0.4%), m.p. 98°, reported¹⁸ m.p. 98°. The infrared spectrum was identical with that of an authentic sample and there was no depression of mixed melting point.

The residue in the reaction flask was boiled with benzene and a small amount of benzene-insoluble, water-soluble solid (3.2 g.) was separated by filtration. The filtrate was evaporated to a small volume and chilling separated triphenylphosphine oxide (42.5 g., 0.15 mole, 75%).

Treatment of Dichloroacetoneitrile with Hydrogen Chloride.—Dichloroacetoneitrile (2.5 g., 0.0023 mole) was introduced into a Dry Ice trap and the trap was immersed in a Dry Ice-bath. Anhydrous hydrogen chloride was passed through the trap for 15 min. and the trap was removed from the Dry Ice-bath. The fuming liquid in the trap had an infrared spectrum quite similar to that of the fuming liquid produced from the reaction of triphenylphosphine and 2,2,2-trichloroacetamide. The residual liquid in the trap solidified on standing. The solid was dissolved in methylene chloride and the solution was evaporated to a small volume. The addition of hexane separated 2,2-dichloroacetamide, m.p. 98°.

N-Methyl-N-phenyl-1,2,2-trichlorovinylamine (VIII).—A mixture of N-methyl-2,2,2-trichloroacetanilide (50.4 g., 0.20 mole), triphenylphosphine (52.4 g., 0.20 mole) and benzene (200 ml.) was heated at 85° for 2 hr. The benzene was evaporated *in vacuo* and distillation produced N-methyl-N-phenyl-1,2,2-trichlorovinylamine as a colorless liquid (28.3 g., 0.12 mole, 60%), b.p. 105° (0.5 mm.), n_D^{25} 1.5859.

Anal. Calcd. for $C_9H_9Cl_3N$: C, 45.70; H, 3.41; N, 5.92; Cl, 44.97. Found: C, 45.88; H, 3.53; N, 6.05; Cl, 44.59.

The residue was dissolved in hot benzene and the solution was evaporated to a small volume. Chilling separated triphenylphosphine oxide (52.6 g., 0.19 mole, 95%).

A solution of N-methyl-N-phenyl-1,2,2-trichlorovinylamine (VIII, 1.70 g., 0.0072 mole) in acetone (10 ml.) and water (20 ml.) was refluxed for 2 hr. and the resulting mixture was extracted with benzene (50 ml.). The benzene solution was dried over anhydrous magnesium sulfate and evaporated to a small volume. The addition of hexane and chilling separated N-methyl-2,2-dichloroacetanilide (1.37 g.,

(11) The boiling points and melting points reported are uncorrected.

(12) J. Braun, F. Jostes and W. Munch, *Ann.*, **453**, 133, 146 (1927).

(13) G. M. Kosalopoff, *J. Am. Chem. Soc.*, **72**, 5508 (1950).

(14) T. Zinke and O. Kegel, *Ber.*, **23**, 243 (1890).

(15) O. Wallach, *Ann.*, **214**, 223 (1882).

(16) L. Besshopinick, *Ber.*, **6**, 732 (1873).

(17) A sample from Aldrich Chemical Co. was distilled.

(18) A. Pinner and F. Fuchs, *Ber.*, **10**, 1066 (1877).

0.0063 mole, 88%), m.p. 70° reported¹⁹ m.p. 69.9°. The infrared spectrum was identical with that of an authentic sample and there was no depression of mixed melting point.

N,N-Diethyl-2,2-dichloro-2-fluoroacetamide (IXa).—A solution of diethylamine (60.0 g., 0.81 mole) in benzene (100 ml.) was stirred while a solution of dichlorofluoroacetic anhydride (55.2 g., 0.2 mole) in hexane (100 ml.) was added dropwise. The solvents were removed *in vacuo* and distillation gave N,N-diethyl-2,2-dichloro-2-fluoroacetamide (28.3 g., 0.14 mole, 70%), b.p. 108–110° (32 mm.), n_D^{20} 1.4544.

Anal. Calcd. for $C_8H_{10}Cl_2FNO$: C, 35.66; H, 5.00; N, 6.93; Cl, 35.09. Found: C, 35.71; H, 5.13; N, 6.97; Cl, 34.84.

N,N-Diethyl-1,2-dichloro-2-fluorovinylamine (Xa).—A solution of N,N-diethyl-2,2-dichloro-2-fluoroacetamide (40.2 g., 0.20 mole) and tributylphosphine (40.4 g., 0.20 mole) was heated in a nitrogen atmosphere at 125–130° for 2 hr. Distillation produced N,N-diethyl-1,2-dichloro-2-fluorovinylamine (4.9 g., 0.026 mole, 13%), b.p. 34–35° (4.3 mm.), n_D^{20} 1.4462.

Anal. Calcd. for $C_8H_{10}Cl_2FN$: C, 38.73; H, 5.42; N, 7.53; Cl, 38.11. Found: C, 38.88; H, 5.40; N, 7.52; Cl, 38.17.

Further distillation of the reaction mixture gave N,N-diethyl-2,2-dichloro-2-fluoroacetamide (14.5 g.), b.p. 58–62° (1.5 mm.), n_D^{20} 1.4535. The infrared spectrum was identical with that of the sample prepared as described previously.

The distillation residue was extracted with a mixture of water (200 ml.) and benzene (200 ml.). The benzene portion was dried over anhydrous magnesium sulfate and the benzene was removed *in vacuo*. Distillation gave somewhat impure N,N-diethyl-2,2-dichloro-2-fluoroacetamide (6.0 g., total 20.5 g., 51%), b.p. 44–46° (0.15 mm.). The infrared spectrum was essentially identical with that of the sample prepared as described previously. Further distillation gave tributylphosphine oxide (19.7 g., 0.09 mole, 45%), b.p. 125° (0.4 mm.). The infrared spectrum was identical with that of an authentic sample.

The aqueous extract was treated with charcoal and extracted with chloroform. The aqueous portion gave a positive test for chloride ion. The chloroform extract was dried over anhydrous magnesium sulfate and the chloroform was evaporated leaving a brownish oil. The infrared spectrum of the oil (3% $CHCl_3$) exhibited significant absorptions at 4.07 and 6.12 μ .

A small portion of the enamine Xa was treated with water (10 ml.) and the mixture was extracted with ether (50 ml.). The aqueous solution gave a positive test for chloride ion. The ethereal solution was dried over anhydrous magnesium sulfate and the ether was evaporated. Distillation produced N,N-diethyl-2-chloro-2-fluoroacetamide n_D^{20} 1.4520.

Anal. Calcd. for $C_6H_{11}ClFNO$: C, 42.99; H, 6.62; N, 8.37; Cl, 21.15. Found: C, 42.95; H, 6.55; N, 8.13; Cl, 21.16.

N,N-Diethyl-2,2-dichloropropionamide (IXb).—A mixture of 2,2-dichloropropionic acid (61.0 g., 0.43 mole) and thionyl chloride (90.0 g., 0.76 mole) was refluxed for 2 hr. The excess thionyl chloride was evaporated *in vacuo*, benzene (100 ml.) was added to the residue and the solution was chilled to 0°. Diethylamine (63.0 g., 0.85 mole) in benzene (100 ml.) was added dropwise with stirring. Benzene (100 ml.) was added and the mixture was refluxed for 0.5 hr. The resulting solution was washed with water (2 × 100 ml.), 10% sodium hydroxide solution (150 ml.) and again with water (200 ml.). The benzene solution was dried over anhydrous magnesium sulfate and the benzene was evaporated *in vacuo*. Distillation gave N,N-diethyl-2,2-dichloropropionamide (37.0 g., 0.19 mole, 44%), b.p. 47–52° (0.3–0.45 mm.). n_D^{20} 1.4714.

Anal. Calcd. for $C_7H_{13}Cl_2NO$: C, 42.44; H, 6.61; N, 7.07; Cl, 35.80. Found: C, 42.76; H, 6.31; N, 7.92; Cl, 35.15.

Reaction of N,N-Diethyl-2,2-Dichloropropionamide with Tributylphosphine.—A mixture of N,N-diethyl-2,2-dichloropropionamide (9.9 g., 0.05 mole) and tributylphosphine (10.1 g., 0.05 mole) was heated at 160–170° for 1 hr. Distillation gave N,N-diethyl-2,2-dichloropropionamide

(2.4 g., 14%), b.p. 52–54° (0.5 mm.), and a second fraction (3.0 g.), b.p. 54–100°, which appeared to be a mixture of the amide, tributylphosphine and tributylphosphine oxide (by infrared analysis). A portion of the residue was washed with ether and dried *in vacuo*. The residue was found to be water soluble and the aqueous solution gave a positive test for chloride ion. The infrared spectrum of the residue (3% $CHCl_3$) showed significant absorption at 4.05 and 6.12 μ .

N,N-Diethyl-2,2-dichlorophenylacetamide (IXd). **A. From Phenylglyoxylic Acid.**—A slurry of phosphorus pentachloride (54 g., 0.26 mole) in benzene (150 ml.) was stirred while a solution of phenylglyoxylic acid (20.0 g., 0.15 mole) in methylene chloride (100 ml.) was added. The resulting mixture was refluxed for 1 hr. The solvents and phosphorus oxychloride were distilled *in vacuo* and the residue was refluxed at 100° for 1 hr. Methylene chloride (150 ml.) was added and then a solution of diethylamine (40.0 g., 0.55 mole) in methylene chloride (100 ml.) was added dropwise with stirring. The resulting solution was washed with water (200 ml.) and dried over calcium chloride. Filtration and evaporation of the solvent left a brownish oil. Distillation produced a liquid, b.p. 80–130° (0.4–1.0 mm.). Redistillation gave a colorless liquid (4.5 g.), b.p. 108–112° (1.2 mm.), n_D^{20} 1.4936, and N,N-diethyl-2,2-dichlorophenylacetamide (13.2 g., 0.05 mole, 33%), b.p. 136–140° (0.3–0.35 mm.), n_D^{20} 1.5430.

Anal. Calcd. for $C_{12}H_{13}Cl_2NO$: C, 55.40; H, 5.81; N, 5.39; Cl, 27.25. Found: C, 56.33; H, 6.01; N, 5.09; Cl, 26.60.

B. From Phenylacetyl Chloride.—A mixture of phosphorus pentachloride (84.0 g., 0.4 mole) and phenylacetyl chloride (31.0 g., 0.2 mole) was refluxed at 140°. The reflux temperature slowly decreased as phosphorus trichloride was formed. After refluxing 24 hr., distillation gave phosphorus trichloride (18 g.), b.p. 74–76°. The residue was again refluxed for 24 hr. and distillation gave phosphorus trichloride (17 g.). The residue was refluxed for an additional 24 hr. and distillation gave phosphorus trichloride (6 g., total 41 g., 0.3 mole, 75%). Further distillation gave a forerun and then the acid chloride as a colorless liquid (40.5 g., 0.18 mole, 90%), b.p. 102–105° (6.5–7 mm.), n_D^{20} 1.5490.

Anal. Calcd. for $C_8H_8Cl_2O$: C, 42.88; H, 2.25; Cl, 47.38. Found: C, 42.99; H, 2.44; Cl, 47.62.

A solution of the acid chloride (13.0 g., 0.058 mole) in benzene (50 ml.) was stirred while diethylamine (8.5 g., 0.116 mole) was added dropwise. Benzene (100 ml.) was added and the mixture was washed with water (2 × 100 ml.). The benzene solution was dried over calcium chloride and the benzene was evaporated *in vacuo*. Distillation of the residue gave a yellow liquid (9.6 g.), b.p. 137–144° (1.2 mm.). Redistillation gave a forerun (1.2 g.), b.p. 137–140° (1.2 mm.), and then N,N-diethyl-2,2-dichlorophenylacetamide (7.6 g., 0.029 mole, 50%), b.p. 142–144° (1.3 mm.), n_D^{20} 1.5443. The infrared spectrum was identical with that of the sample prepared as described previously. Vapor phase analysis indicated the presence of only one major component.

N,N-Diethyl- α,β -Dichloro- β -styrylamine (X). **A. With Tributylphosphine.**—N,N-Diethyl-2,2-dichlorophenylacetamide (5.2 g., 0.02 mole) and tributylphosphine (4.1 g., 0.02 mole) were heated at 100° for 0.5 hr. in a nitrogen atmosphere. Distillation produced N,N-diethyl- α,β -dichloro- β -styrylamine (3.3 g., 0.014 mole, 70%), b.p. 110–119° (1.1 mm.), n_D^{20} 1.5504.

Anal. Calcd. for $C_{12}H_{13}Cl_2N$: C, 59.03; H, 6.19; N, 5.74. Found: C, 59.59; H, 6.83; N, 6.63.

Further distillation gave tributylphosphine oxide (4.0 g., 0.018 mole, 90%).

B. With Triphenylphosphine.—A mixture of N,N-diethyl-2,2-dichlorophenylacetamide (10.2 g., 0.04 mole) and triphenylphosphine (10.5 g., 0.04 mole) was heated for 0.75 hr. at 110°. Distillation gave a yellow liquid which on redistillation gave N,N-diethyl- α,β -dichloro- β -styrylamine (4.7 g., 0.019 mole, 48%), b.p. 98–103° (0.5–0.6 mm.), n_D^{20} 1.5504. The infrared spectrum was identical with that of the sample prepared as described previously. Vapor phase analysis indicated the presence of only one component. The distillation residue was dissolved in hot methylene chloride and the solution was placed on a column of alumina

(19) P. McKie, *J. Chem. Soc.*, **123**, 2215 (1923).

packed wet with hexane. Elution with benzene and recrystallization from benzene-hexane gave triphenylphosphine oxide (6.6 g., 0.024 mole, 60%).

A mixture of *N,N*-diethyl- α,β -dichlorostyrylamine (3.15 g., 0.0129 mole) and water (20 ml.) was shaken in a stoppered flask for 4 hr. The resulting mixture was extracted with methylene chloride (2 \times 50 ml.) and the aqueous portion was found to contain chloride ion (0.0126 mole, 97%, by potentiometric titration). The methylene chloride extract was dried over anhydrous magnesium sulfate and the methylene chloride was evaporated. Distillation of the residue gave *N,N*-diethyl- α -chlorophenylacetamide (2.62 g., 0.0116 mole, 90%), b.p. 129–133° (0.45–0.5 mm.). The product solidified on standing; m.p. 50–51°.

Anal. Calcd. for $C_{12}H_{16}ClNO$: C, 63.85; H, 7.15; N, 6.21; Cl, 15.71. Found: C, 63.99; H, 7.01; N, 6.15; Cl, 15.84.

***N,N*-Diethylcinnamamide.**—A solution of *N,N*-diethyl-2-chloroacetamide (14.95 g., 0.10 mole) and tributylphosphine (20.25 g., 0.10 mole) in benzene (150 ml.) was refluxed in a nitrogen atmosphere for 1.5 hr. A small portion of the solution was removed and the benzene was evaporated leaving a light yellow viscous residue. The residue was washed with ether (2 \times 50 ml.) and dried *in vacuo*. The infrared spectrum of the residue (3% $CHCl_3$) showed significant absorption at 6.14 and 4.05 μ .

The major portion of the benzene solution was chilled in an ice-bath and an ethereal solution of phenyllithium (1.18 *M*, 90 ml., 0.106 mole C_6H_5Li) was added dropwise. The solution was stirred for 10 min. and benzaldehyde (10.6 g., 0.1 mole) was added dropwise with stirring. The solution was allowed to stand for 24 hr. and then was filtered to remove the precipitated lithium chloride. The filtrate was placed on a column of Fisher A-540 alumina packed wet with hexane. Elution and recrystallization with hexane gave *trans-N,N*-diethylcinnamamide (16.1 g., 0.079 mole, 79%), m.p. 72–73°, reported²⁰ m.p. 72°. The infrared spectrum was identical with that of an authentic sample and there was no depression of mixed melting point. Evaporation of the hexane mother liquor left an oil (0.48 g.) with an infrared spectrum similar to, but different from, that of the above product (perhaps the *cis* isomer). Elution with benzene gave impure tributylphosphine oxide.

Tetrabutylphosphonium Bromide.—Tributylphosphine (8.0 g., 0.04 mole) was added to butyl bromide (100 g., 0.74 mole) dropwise, with stirring, in a nitrogen atmosphere. The solution was stirred for 2 hr. and the excess butyl bromide was removed *in vacuo*. The resulting white solid was slurried with ether and filtered. Recrystallization from acetone-ether gave tetrabutylphosphonium bromide (6.2 g., 0.018 mole, 45%), m.p. 102–104°.

Anal. Calcd. for $C_{16}H_{36}BrP$: C, 56.63; H, 10.69. Found: C, 56.51; H, 10.59.

***N,N*-Diphenyl-1,2-dichlorovinylamine (XIIIb).**—A mixture of *N,N*-diphenyl-2,2-dichloroacetamide (7.0 g., 0.025 mole) and triphenylphosphine (6.5 g., 0.025 mole) was heated with stirring at 125° for 0.5 hr. Distillation gave a yellowish liquid which on redistillation gave *N,N*-diphenyl-1,2-dichlorovinylamine (5.5 g., 0.021 mole, 84%), b.p. 154–158° (0.5 mm.), n_D^{25} 1.6300.

Anal. Calcd. for $C_{14}H_{11}Cl_2N$: C, 63.65; H, 4.20; N, 5.34; Cl, 26.84. Found: C, 63.52; H, 4.41; N, 5.39; Cl, 26.90.

The solid residue was dissolved in methylene chloride and the solution was treated with charcoal. Evaporation to a small volume and the addition of hexane separated triphenylphosphine oxide (5.5 g., 0.020 mole, 80%).

N,N-Diphenyl-1,2-dichlorovinylamine (0.40 g., 0.0015 mole) was allowed to stand in water (10 ml.) in a stoppered flask for 12 hr. The resulting mixture was extracted with ether (50 ml.). The aqueous portion gave a positive test for chloride ion. The ethereal solution was dried over anhydrous magnesium sulfate and evaporated to a small volume. The addition of hexane separated *N,N*-diphenyl-2-chloroacetamide (0.25 g., 0.0010 mole, 67%), m.p. 117–118°, reported²¹ m.p. 116°. The infrared spectrum was identical with that of an authentic sample and there was no depression of mixed melting point.

(20) N. H. Cromwell and J. A. Coughlan, *J. Am. Chem. Soc.*, **67**, 903 (1945).

(21) H. Clark, *J. Chem. Soc.*, **97**, 429 (1910).

***N*-Phenyl-2-chloroacetimidoyl Chloride.**—A mixture of 2,2-dichloroacetanilide (10.2 g., 0.050 mole) and tributylphosphine (10.1 g., 0.050 mole) was heated and stirred in a nitrogen atmosphere. At 70° an exothermic reaction increased the temperature to 130°. The reaction was moderated with an ice-bath and after the temperature had dropped to 50° the solution was heated at 80–90° for 0.5 hr. Distillation produced a yellow oil, b.p. 140–144° (10 mm.), which on redistillation gave *N*-phenyl-2-chloroacetimidoyl chloride (3.3 g., 0.018 mole, 36%), b.p. 73–75° (0.45 mm.), n_D^{25} 1.5677.

Anal. Calcd. for $C_8H_7Cl_2N$: C, 51.09; H, 3.75; N, 7.45; Cl, 37.71. Found: C, 51.11; H, 3.85; N, 7.50; Cl, 37.77.

Further distillation of the reaction mixture gave tributylphosphine oxide (4.2 g., 0.019 mole, 38%).

Reaction of *N*-Methyl-2,2-dichloroacetanilide and Tributylphosphine.—A mixture of *N*-methyl-2,2-dichloroacetanilide (10.3 g., 0.047 mole) and tributylphosphine (10.2 g., 0.05 mole) was heated at 100° for 1 hr. in a nitrogen atmosphere. Distillation produced a yellow liquid (2.7 g.), n_D^{25} 1.5647. Redistillation gave *N*-methyl-*N*-phenyl-1,2-dichlorovinylamine (XIIIc, 1.6 g., 0.008 mole, 17%), b.p. 84–89° (1.1 mm.). The infrared spectrum of the product exhibited carbon-carbon double bond absorption at 6.3 μ . The enamine rapidly decomposed to a red-brown tar on standing.

A small amount of the product was treated with water and the aqueous mixture was extracted with ether. The aqueous portion gave a positive test for chloride ion. The ethereal extract was dried over anhydrous magnesium sulfate and most of the ether was evaporated. The addition of hexane separated *N*-methyl-2-chloroacetanilide, m.p. 69–70°, reported²² m.p. 70°. The infrared spectrum was identical with that of an authentic sample and there was no depression of mixed melting point.

Continued distillation of the reaction mixture gave a colorless liquid (6.0 g.), b.p. 125–130° (1.2 mm.). The infrared spectrum of the liquid indicated that it was a mixture of the starting amide and tributylphosphine oxide. Treatment of the liquid with 50% hydrochloric acid (25 ml.) and chilling separated *N*-methyl-2,2-dichloroacetanilide (4.2 g., 0.02 mole, 43%), m.p. 69–70°. The infrared spectrum was identical with that of an authentic sample. The distillation residue was treated with hot ethyl acetate and filtration produced a yellow solid. Recrystallization from chloroform-ethyl acetate gave *N*-methylanilinoethylene-1,2-bis-(tributylphosphonium) chloride (XIV, 2.1 g., 0.0034 mole, 7%), m.p. 234–235°.

Anal. Calcd. for $C_{33}H_{63}Cl_2NP_2$: C, 65.33; H, 10.46; N, 2.31; P, 10.21; Cl, 11.69. Found: C, 64.48; H, 10.23; N, 3.06; P, 10.06; Cl, 11.52; Cl, 11.8.

***N*-Methylanilinoethylene-1,2-bis-(tributylphosphonium) Chloride (XIV).**—A solution of *N*-methyl-2,2-dichloroacetanilide (20.6 g., 0.1 mole) and tributylphosphine (60.6 g., 0.3 mole) in benzene (50 ml.) was heated at 125° in a nitrogen atmosphere for 2.5 hr. The mixture was cooled and ethyl acetate (200 ml.) was added. The mixture was warmed, stirred and chilled. Filtration and recrystallization from chloroform-ethyl acetate produced *N*-methylanilinoethylene-1,2-bis-(tributylphosphonium) chloride as yellow crystals (33.0 g., 0.054 mole, 54%), m.p. 234–235°. The infrared spectrum was identical with that of the sample prepared as described previously.

Reaction of *N*-Methylanilinoethylene-1,2-bis-(tributylphosphonium) Chloride and Sodium Hydroxide Solution.—A solution of *N*-methylanilinoethylene-1,2-bis-(tributylphosphonium) chloride (20.0 g., 0.033 mole) and sodium hydroxide (2.7 g., 0.067 mole) in water (95 ml.) was allowed to stand for 72 hr. The resulting mixture was extracted with methylene chloride (2 \times 100 ml.) and the extract was dried over calcium chloride. The methylene chloride was evaporated and distillation gave *N*-methylaniline (2.0 g., 0.018 mole, 54%), b.p. 60° (1.5 mm.). The infrared spectrum was identical with that of an authentic sample. Further distillation gave tributylphosphine oxide (7.9 g., 0.039 mole, 51%).

***N*-Ethylbenzimidoyl Chloride (XXVI).** **A. From *N*-Chloro-*N*-ethylbenzamide and Triphenylphosphine.**—A solution of *N*-chloro-*N*-ethylbenzamide²³ (8.0 g., 0.044 mole)

(22) W. Grothe, *Arch. Pharm.*, **233**, 591 (1900).

(23) E. Slosson, *Am. Chem. J.*, **29**, 309 (1903).

in benzene (50 ml.) was stirred while a solution of triphenylphosphine (11.4 g., 0.043 mole) in benzene (50 ml.) was added at such a rate that the temperature remained below 40°. The solution was heated at 50° for 15 min. and the benzene was removed *in vacuo*. Distillation produced a colorless liquid which on redistillation gave N-ethylbenzimidoyl chloride (2.7 g., 0.016 mole, 37%), b.p. 89–91° (9 mm.), n_D^{25} 1.5508; reported²⁴ b.p. 110–111° (15 mm.). The distillation residue was dissolved in hot benzene. Chilling and the addition of hexane separated triphenylphosphine oxide (11.0 g., 0.040 mole, 93%).

B. From N-Ethylbenzamide and Phosphorus Pentachloride.²⁴—A solution of N-ethylbenzamide (7.5 g., 0.05 mole) and phosphorus pentachloride (10.4 g., 0.05 mole) in benzene was heated at 50° for 1 hr. The benzene and phosphorus oxychloride were removed *in vacuo* and distillation gave a yellow liquid which on redistillation gave N-ethylbenzimidoyl chloride (3.7 g., 0.022 mole, 44%), b.p. 51° (0.25 mm.), n_D^{25} 1.5507. The infrared spectrum was identical with that of the sample prepared as described in part A.

Reaction of N,N-Diethyl-2,2,2-Trichloroacetamide with Tributylphosphine in the Presence of tetrapropylammonium Bromide.—A solution of tetrapropylammonium bromide (26.6 g., 0.10 mole) and N,N-diethyl-2,2,2-trichloroacetamide (21.9 g., 0.10 mole) in chloroform (150 ml.) was stirred while tributylphosphine (30.3 g., 0.15 mole) was added dropwise in a nitrogen atmosphere. The solution was heated at 85° for 7 hr. and then the chloroform was removed

in vacuo. Distillation gave two arbitrary fractions, I, 7.5 g., b.p. 25–64° (0.3 mm.), and II, 17.6 g., b.p. 64–130° (0.3–0.7 mm.). Fractions I and II were found to contain less than 1% bromine, if any.⁸ Vapor phase and infrared analysis of the fractions showed them to contain: N,N-diethyl-1,2,2-trichlorovinylamine¹ (3.2 g., 0.016 mole, 16%), tributylphosphine (11.5 g., 0.057 mole, 38%), N,N-diethyl-2,2,2-trichloroacetamide (1.8 g., 0.0082 mole, 8%), an unknown (1.8 g.) and tributylphosphine oxide (6.2 g., 0.028 mole, 28%). The unknown substance decomposed before it could be characterized.

The residue was extracted with hexane (100 ml. and evaporation of the hexane gave impure tributylphosphine oxide. Extraction of the residue with ethyl acetate separated a tan solid. Recrystallization from acetone-ethyl acetate gave somewhat impure tetrapropylammonium bromide (25.4 g., 0.095 mole, 95%), m.p. 245–254°, reported²⁵ m.p. 252°. The infrared spectrum was essentially identical with that of an authentic sample.

Reaction of N,N-diethyl-2,2,2-trichloroacetamide and Tributylphosphine in Chloroform.—A solution of N,N-diethyl-2,2,2-trichloroacetamide (21.9 g., 0.10 mole) in chloroform (150 ml.) was stirred in a nitrogen atmosphere while tributylphosphine (30.3 g., 0.15 mole) was added dropwise. The solution was heated at 70° for 3 hr. and the chloroform was evaporated *in vacuo*. Distillation produced N,N-diethyl-1,2,2-trichlorovinylamine¹ (11.5 g., 0.057 mole, 57%), n_D^{25} 1.4864.

(25) S. Sugden and H. Wilkins, *ibid.*, **132**, 1297 (1929); Eastman Kodak Co. sample decomposed at 267–269°.

(24) G. Lander, *J. Chem. Soc.*, **83**, 320 (1903).

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION, ST. LOUIS, MO.]

N.m.r. Study of the P–C(OH)–P to P–C–O–P Rearrangement: Tetraethyl 1-Hydroxyalkylidenediphosphonates¹

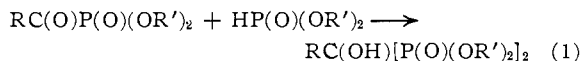
BY STEVEN J. FITCH AND KURT MOEDRITZER

RECEIVED JANUARY 9, 1962

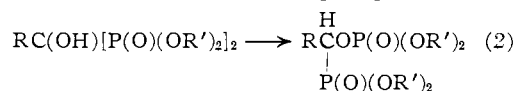
Compounds previously reported to be tetraalkyl 1-hydroxyalkylidenediphosphonates are found to be isomeric rearrangement products of the reported materials. Authentic tetraethyl 1-hydroxyethylidenediphosphonate was prepared, and its rearrangement was demonstrated. P³¹ and H¹ n.m.r. spectra, infrared spectra and chemical evidence are presented in support of the rearrangement, and the rearrangement is related to other reactions of 1-hydroxyalkylphosphonates.

Introduction

The synthesis of 1-hydroxyalkylidenediphosphonate esters by the base-catalyzed addition of dialkyl phosphonates to dialkyl acylphosphonates has been reported.^{2a,b} However, our attempts to



prepare diphosphonates by the reported methods led to the formation of isomeric compounds containing two chemically different kinds of phosphorus atoms. This finding was interpreted as meaning that the initially formed diphosphonates had rearranged to the isomeric phosphates. Sub-



sequently, authentic tetraethyl 1-hydroxyethylidenediphosphonate was isolated and characterized, and direct evidence of its rearrangement was obtained.

(1) Presented at 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) (a) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4450 (1956); (b) J. A. Cade, *J. Chem. Soc.*, 2272 (1959).

Results and Discussion

P¹³ N.m.r. Spectra.—The distilled products of reaction 1 with R = CH₃ or C₆H₅ and R' = C₂H₅ give spectra having two peaks of approximately equal size, showing that equal numbers of phosphorus atoms are in the two chemical states. The chemical shift of one peak is about +1 p.p.m., which is characteristic of trialkyl orthophosphate esters.³ The other peak occurs at –16 (R = C₆H₅) or –21 (R = CH₃) p.p.m. As can be seen from Table I, this second chemical shift is appropriate for a diethyl alkylphosphonate having

TABLE I

CHANGE IN CHEMICAL SHIFT OF RP(O)(OC₂H₅)₂ WITH INCREASING ELECTRONEGATIVITY OF α-SUBSTITUENTS^a

R	Chemical shift, p.p.m.	R	Chemical shift, p.p.m.
C ₂ H ₅	–32.5	ClCH ₂	–18
CH ₃	–30	Cl ₂ CH	–9.3
n-C ₉ H ₁₉ CH(OH)	–25.5	Cl ₃ C	–6.5
C ₂ H ₅ O ₂ CCH ₂	–19		

^a These chemical shifts are abstracted from ref. 3 and from unpublished data in this Laboratory.

(3) J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).